

Isolation and Characterization of Amphoteric Components of SHRP Asphalts by Ion Exchange Chromatography

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ABSTRACT

An ion exchange chromatography separation procedure was devised for the purpose of isolating compounds of amphoteric nature from four asphalts studied in the Strategic Highway Research Program. Amphoteric materials constitute about 18-25% of the asphalts studied. Other defined chemical fractions (neutral, acidic, and basic fractions) also were collected. Of the four fractions, the amphoteric is the most polar and most aromatic in each of the asphalts. Number-average molecular weights of the amphoteric fractions are two-to-four times greater than those of the parent asphalts.

Several mixtures of the above ion exchange chromatography fractions with each other and with whole asphalts were prepared and their viscosities were measured. Based on these studies, amphoterics are the chemical component of asphalts most responsible for high viscosities. Polyfunctional compounds that are of purely acidic or basic character do not appear to be present in large amounts.

INTRODUCTION

One model of asphalt structure proposes that asphalts can be considered to be dispersions of polar, aromatic molecules in solvent moieties consisting of less polar, more aliphatic molecules (1). The relative amount of polars and the effectiveness by which they are solubilized will be major determinants of asphalt properties (2). If this model is correct, polyfunctional polar molecules should contribute disproportionately to the buildup of molecular associations, which presumably govern such asphalt bulk properties as viscosity. Polyfunctional molecules may be categorized as amphoteric, polyacidic, or polybasic. It should be possible to isolate these materials and study their properties if the model described above is correct.

The technique of ion exchange chromatography (IEC) has been used to separate tar sand bitumens, shale oils, crude oils and their components into defined chemical fractions (3-9). When used to separate the above mentioned substrates, IEC works as a form of affinity chromatography. Usually, neutral, acidic, and basic fractions of varying strengths are collected. An IEC separation method used for the separation of asphalts studied in the

Strategic Highway Research Program (SHRP) into neutral, acidic, and basic fractions (4, 5) was modified to separate asphalts into neutral, acid, base, and amphoteric fractions.

EXPERIMENTAL

The experimental details of the IEC separation of asphalts, including resin activation, have been published (4, 5). In the conventional IEC separation, solutions of asphalts in either a mixed solvent (benzene, tetrahydrofuran, ethanol) or cyclohexane are pumped through two columns, the first filled with activated anion resin, and the second filled with activated cation resin. For the separation of amphoterics, a solution of asphalt (16 g) in cyclohexane (64 mL) was pumped into a jacketed column filled with activated cation resin (Bio-Rad MP-50, 100-200 mesh). All molecules with one or more basic functional groups are adsorbed on the cation resin. Molecules containing only acidic or no functional groups are eluted, and these eluates are pumped through a jacketed column filled with activated anion resin (Bio-Rad MP-1, 100-200 mesh). Acidic materials are adsorbed on the anion resin, and neutral materials are eluted. Column temperatures of 37°C (98.6°F) are maintained by circulating warm water through the column jackets. Both columns are desorbed in the manner previously described (4, 5). The materials desorbed from the cation resin are divested of solvent and are redissolved in cyclohexane. This solution is pumped through another jacketed column filled with activated anion resin. Amphoteric materials are collected on the anion resin, and basic materials are eluted. The base fraction is recovered by solvent removal, and the amphoterics are recovered by desorption of the anion resin by formic acid-benzene, followed by solvent removal. A flow sheet for this process is illustrated in Figure 1.

To make mixtures of asphalts and IEC fractions or mixtures of IEC fractions, materials are added to a tared vial and methylene chloride is added to the mixture. The sample is allowed to stand overnight under argon. The mixture then is rotated on a rotary evaporator immersed in the waterbath at a temperature of 44°C (111.2°F). After most of the methylene chloride has evaporated off, the temperature is increased until boiling of the water is observed in the bath. Vacuum then is applied to the sample, approximately 208 mm Hg (8.19 in Hg). The vacuum is increased gradually to prevent any bubbling of the sample. A maximum vacuum of approximately 4.7 mm Hg (0.19 in Hg) is reached and the sample is allowed to rotate for 2 hours. The sample is then immersed into an oil bath of 125°C (257°F) for 2 hours at 2 torr (0.08 in Hg). The dried samples are submitted for rheological analysis.

Elemental analyses were performed by the Analytical Research Division of Western Research Institute, using standard methods. Number-average molecular weights (\bar{M}_n) were determined by vapor phase osmometry (VPO) in toluene or pyridine at 60°C (140°F) using ASTM Method D2503. Infrared functional group (IR-FGA) analyses were obtained on a Perkin-Elmer 983G infrared spectrophotometer using a method developed by Petersen (10). Rheological data were obtained on a Rheometrics mechanical spectrometer. Samples were annealed prior to measurement at 150°C (302°F) for one hour under an inert gas atmosphere. Measurements were performed within two hours after the samples had cooled to room temperature.

Liquid-state ^1H and ^{13}C NMR measurements were made on a JEOL GSX-270 NMR spectrometer. The experimental conditions for recording a ^1H spectrum were 8 scans, a pulse width of 5.4 μs (45°), an acquisition time of 1.5 s, a pulse delay of 20 s, and 16 K time-domain data points. The conditions for recording a ^{13}C NMR spectrum were 320 scans, 9.3 μs pulse width (90°), 0.8 s acquisition time, a pulse delay of 10 s, 32 K time-domain data points, and gated decoupling with the decoupler on during data acquisition. Carbon-13 spectra were obtained on samples containing ~ 0.05 M chromium (III) acetylacetonate as a relaxation agent.

DISCUSSION

Yields of amphoteric, base, acid, and neutral fractions from IEC separation of four SHRP asphalts (coded AAD-1, AAG-1, AAK-1, and AAM-1) are listed in Table 1. For some runs, neutrals were not subsequently separated from acids, so the combination of the two materials is listed under the entry neutral plus acids. In some other runs, amphoteric were not subsequently separated from bases, so this combination of materials is listed under the entry amphoteric plus bases. In each case, the neutral fraction comprises over half of the mass of the asphalt. Yields of neutral materials are similar to those reported using another IEC separation method on the same asphalts (4, 5). Of the three polar fractions, the amphoteric is by far the largest for each of the asphalts. The amphoteric materials are black solids which swell when contacted with small amounts of solvent. Bases and acids are tacky semisolids. Neutrals are viscous liquids.

Number-average molecular weights (\bar{M}_n) of amphoteric and bases are listed in Table 2. The \bar{M}_n values of the amphoteric fractions vary from 1,540 Daltons (AAG-1) to 3,690 Daltons (AAK-1) in toluene, and from 1,240 Daltons (AAG-1) to 2,730 Daltons (AAK-1) in pyridine. The lower \bar{M}_n values in pyridine compared with toluene indicate that amphoteric materials tend to form associations. The \bar{M}_n values of the base fractions range from 815-880 Daltons (AAG-1) to 1,740 Daltons (AAM-1), and are the same in toluene and pyridine, indicating that by themselves the total base fractions do not engage in strong associations. The \bar{M}_n values of the parent asphalts are: AAD-1, 700 Daltons; AAG-1, 710 Daltons, AAK-1, 860 Daltons, and AAM-1, 1,300 Daltons (4, 5). These \bar{M}_n values are the same when measured in pyridine or toluene for those asphalts completely soluble in both solvents. Asphalt AAM-1 is not completely soluble in pyridine.

Infrared (IR-FGA) analyses of amphoteric, bases, and the combination of neutrals and acids of four asphalts are reported in Table 3. The bifunctional 2-quinolone compounds are found in abundance only in the four amphoteric fractions. Other polar functional groups measured by the IR-FGA method are distributed among the various fractions, largely according to expectation. Carboxylic acids and phenols are found in measurable amounts in amphoteric and neutral plus acid fractions. Sulfoxides and ketones are concentrated in base fractions. Pyroles are found in measurable amounts in all fractions.

Elemental analyses for carbon, hydrogen, and nitrogen of the four amphoteric fractions (Table 4) show that these materials are aromatic and contain large amounts of nitrogen. Some of the nitrogen atoms are part of basic functional groups (11). Standard deviations of the

elemental analyses of the amphoteric fractions generally are small. Nuclear magnetic resonance (NMR) measurements (Table 5) show that about 40-50% of carbon atoms in the amphoteric fractions are part of aromatic structures, whereas aromatic hydrogens comprise only 6-13% of the total hydrogen, suggesting the presence of condensed aromatic structures.

All the above observations demonstrate that the amphoteric fractions of the four asphalts consist of polar, aromatic molecules which are of relatively high \bar{M}_n compared with the parent asphalts and other IEC fractions (4, 5). These molecules should have the greatest tendencies to associate of all the asphalt IEC fractions, and therefore should be the principal viscosity-enhancing components of asphalts.

In order to test this hypothesis directly, mixtures of each asphalt with each of the four IEC fractions (neutral, amphoteric, acid, and base) were prepared. The compositions of these mixtures were calculated based on the observation that a specific natural abundance of each IEC fraction characterizes each asphalt. For example, asphalt AAD-1 consists of about 54% neutrals, 25% ampherics, 9% bases and 8% acids. Asphalt AAG-1 consists of 52% neutrals, 18% ampherics, 12% bases, and 14% acids. It was decided initially to add ampherics to asphalts such that the resulting mixtures would contain double the natural abundance levels of ampherics. However, the resulting materials were observed to be coal-like, and viscosities were barely measurable at 60°C (140°F). Solvent removal from the prepared mixtures proved to be very tedious. The amphoteric fractions impart great surface activities to the mixtures, and under vacuum, meringues form which flow from distillation flasks into the rotary evaporators used in the solvent removal process.

Accordingly, mixtures for each of the four asphalts were formulated such that ampherics comprise a 50% excess of their natural abundance for each of the asphalts. For example, a 10.0 g sample of AAD-1 contains ~ 2.5 g ampherics, a 25% natural abundance. A 50% excess would be 37.5%. So to make 10.0 g of a mixture having 37.5% ampherics, enough amphoteric material (1.67 g in this case) was added to AAD-1 (8.33 g in this case) to yield 10.0 g of a mixture containing 3.75 g ampherics. For AAG-1, the natural abundance level for ampherics is 18%, much less than for AAD-1. A mixture of AAG-1 containing a 50% excess of this natural abundance would contain 27% ampherics. Similar considerations apply to AAK-1 and AAM-1. Natural abundances of ampherics in these asphalts are similar to those in AAD-1 and AAG-1 respectively.

Mixtures also were formulated by adding neutral, acid, and base fractions to the asphalts. In every case, the same amount of each fraction was added as for the amphoteric fraction. For example, in the AAD-1 mixtures, 1.67 g ampherics was added to 8.33 g AAD-1. In the mixtures of AAD-1 with its neutral fraction, 1.67 g neutrals were added to 8.33 g AAD-1. Similarly, 1.67 g bases were added to 8.33 g AAD-1, and 1.67 g acids were added to 8.33 g AAD-1. The neutral, acid, and base fractions were not added in amounts commensurate with their own natural abundances, but in amounts corresponding to the natural abundance of the amphoteric fraction. This is so that effects of each fraction on rheological properties can be compared on an equivalent mass basis for each asphalt.

Viscosities of all these mixtures at 60°C (140°F) (Table 6) show that, as a fraction, the amphoteric components are the components of the asphalts governing high viscosities, as predicted. Bases cause moderate viscosity increases when added to asphalts and acids cause hardly any increases. These results indicate that there may be few polyfunctional acidic and basic compounds present. Addition of neutral materials causes large viscosity decreases when mixed with parent asphalts. These results do not mean that no viscosity-enhancing species exist in acid, base, or neutral materials, or no viscosity-reducing species exist in the amphoteric fractions. The results apply to the fractions as a whole.

To verify the effect of the absence of amphoteric components on asphalt properties, mixtures of a different kind were prepared. In these mixtures, the relative amounts of neutrals and polars were the same as in the parent asphalts. However amphoteric components have been replaced by bases. In the mixtures discussed earlier, in which IEC fractions are added to whole asphalts, the ratios of neutrals to polars are different from the relative abundance of neutrals and polars in neat asphalts. Acids, bases, and amphoteric components are considered to be the polar fractions. In the new set of mixtures, bases replace amphoteric components, so the mixtures have much more than their natural abundances of bases, but relative amounts of total polars and neutrals are the same as for each of the original four asphalts studied. In Table 7, viscosities at three temperatures and $\tan \delta$ values at 25°C (77°F) of four such mixtures are compared with the same measurements on the parent asphalts. Viscosities of the mixtures are much lower than those of the parent asphalts at all three temperatures. The $\tan \delta$ (ratio of viscous to elastic moduli) values of the mixtures are high, compared with $\tan \delta$ values of parent asphalts, particularly the mixture made up of IEC fractions of AAG-1. The rheological data obtained for these mixtures demonstrate that the amphoteric materials as defined by IEC are largely responsible for viscosity-enhancing phenomena in asphalts.

CONCLUSIONS

Separation of four different asphalts into neutral, acid, base, and amphoteric components by IEC shows that neutral fractions comprise somewhat over half of the asphalts. Amphoteric components are the largest of the three polar fractions. Amphoteric components are much more aromatic than their parent asphalts, and also have higher \bar{M}_n values. These \bar{M}_n values, determined by VPO, are higher in toluene than in pyridine, which indicates that amphoteric components tend to engage in associative interactions.

Mixtures of asphalts with each of the four IEC fractions were prepared and their viscosities measured. Only the mixtures containing amphoteric components were much more viscous than the parent asphalts. Mixtures containing only IEC neutral, acid, and base fractions were much less viscous than parent asphalts and had small values of elastic moduli (based on $\tan \delta$ values) compared with those of parent asphalts. Thus the presence of amphoteric components, presumably forming associations of varying strengths, is required to form elastic networks in asphalts, and asphalt rheological properties should be a function of the nature and relative amounts of amphoteric components present.

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Table 1. Mass Fractions of Amphoteric, Base, Acid, and Neutral Fractions Isolated from Four Asphalts by IEC

Asphalt	Operator (Initials)	IEC Fraction (mass %)					Total Recovery (% of Charge)
		Amphoteric plus Bases	Amphoteric	Bases	Neutrals plus Acids	Acids	Neutrals
AAD-1	MC	25.9		9.3	59.8		95.0
	SK	25.5		9.5	60.4		95.4
	MC	25.0		8.6	62.2		96.7
	SK	25.8		7.7		8.6	96.0
	DG	22.3		12.1		7.3	94.9
Avg. + Std. Dev.		24.9±1.3		9.4±1.5	60.8±1.0	8.0	95.6±0.7
AAG-1	MC	18.6		13.3	66.4		98.3
	SK	18.4		10.7	68.8		98.0
	DG	18.8		12.9		13.4	96.9
	DG	18.2		13.1		15.3	99.5
	Avg. + Std. Dev.	18.5±0.2		12.5±1.0	67.6	14.4	98.2±0.9
AAK-1	MC	24.1		9.6	61.7		95.3
	SK	24.6		10.9	61.5		97.1
	SK	24.2		8.7		8.1	94.8
	DG	23.5		12.9	59.0		95.4
	DG	27.7				7.6	90.5
Avg. + Std. Dev.		24.1±0.4		10.5±1.6	60.7±1.2	7.9	94.6±2.2
AAM-1	MC	18.9		15.6	63.9		98.5
	SK	18.1		12.9	66.1		97.1
	SK	18.9		13.4		10.0	96.3
	DG	34.5				8.5	99.4
	Avg. + Std. Dev.	18.6±0.4		14.0±1.2	65.0	9.3	97.8±1.2

Table 2. Molecular Weights of IEC Amphoteric and Base Fractions

Asphalt	Run No.	Fraction	<u>Molecular Weight (Daltons)</u>	
			Toluene	Pyridine
AAD-1	1	Amphoteric	2,960	2,260
		Base	1,100	1,100
	2	Amphoteric	2,930	2,180
		Base	1,060	1,200
AAG-1	1	Amphoteric	1,540	1,170
		Base	880; 880	-
	2	Amphoteric	1,620	1,240
		Base	815	835
AAK-1	1	Amphoteric	3,690	2,730
		Base	1,260; 1,240	1,340
	2	Amphoteric	3,540	2,160
		Base	1,300	1,350
AAM-1	1	Amphoteric	3,560	insol.
		Base	1,740	insol.
	2	Amphoteric	3,410	insol.
		Base	1,670	insol.

Table 3. Infrared Functional Group Analysis for IEC Amphoteric, Base, and Neutral Plus Acid Fractions of Four Core Asphalts

Asphalt	IEC Fraction	Functional Group Concentration, Moles/L					
		Sulfoxides	Ketones	Carboxylic Acids	2-Quinolones	Pyrrolic N-H	Phenolic O-H
AAD-1	Neutrals Plus Acids	0.05	<0.01	0.01	<0.01	0.2	<0.1
	Bases	0.15	0.17	<0.01	<0.01	0.2	<0.1
	Amphoterics	0.09	<0.01	0.02	0.07	0.4	0.1
AAG-1	Neutrals Plus Acids	0.05	<0.01	0.05	<0.01	0.3	0.1
	Bases	0.08	0.13	<0.01	<0.01	0.2	<0.1
	Amphoterics	0.08	<0.01	0.03	0.07	0.6	0.1
AAK-1	Neutrals Plus Acids	0.08	<0.01	0.02	<0.01	0.1	<0.1
	Bases	0.15	0.10	<0.01	<0.01	0.2	<0.1
	Amphoterics	0.10	<0.01	0.06	0.04	0.3	<0.1
AAM-1	Neutrals Plus Acids	<0.01	<0.01	<0.01	<0.01	0.2	<0.1
	Bases	0.08	0.10	<0.01	<0.01	0.2	<0.1
	Amphoterics	0.06	<0.01	0.02	0.02	0.3	<0.1

Table 4. Carbon, Hydrogen, and Nitrogen Contents of Amphoteric Fractions

Parent Asphalt	Run No.	Element (mass %)			H/C ratio
		C	H	N	
AAD-1	1	80.3	8.6	1.9	1.28
	2	<u>81.1</u>	<u>8.6</u>	<u>1.9</u>	<u>1.26</u>
	Avg.	80.6	8.6	1.9	1.27
AAG-1	1	84.7	8.4	2.5	1.18
	2	84.8	8.6	2.5	1.21
	3	<u>84.8</u>	<u>8.6</u>	<u>2.4</u>	<u>1.21</u>
	Avg. + St. Dev.	84.8 ± 0.1	8.5 ± 0.1	2.5 ± 0.1	1.20 ± 0.01
AAK-1	1	81.5	8.3	1.7	1.21
	2	78.5	8.2	1.6	1.24
	3	81.2	8.2	1.9	1.20
	4	80.9	8.2	2.0	1.19
	5	<u>80.6</u>	<u>8.1</u>	<u>2.0</u>	<u>1.20</u>
	Avg. + Std. Dev.	80.5 ± 1.1	8.2 ± 0.1	1.8 ± 0.2	1.21 ± 0.02
AAM-1	1	88.0	8.5	1.2	1.15
	2	<u>86.4</u>	<u>8.6</u>	<u>1.1</u>	<u>1.19</u>
	Avg.	87.2	8.6	1.2	1.17

Table 5. NMR Analysis of IEC Amphoteric Fractions of Four Core Asphalts

Asphalt	Run No.	% Aromatic Carbon	% Aromatic Hydrogen
AAD-1	1	41.1	7.1
	2	45.0	8.1
AAG-1	1	49.3	11.8
	2	51.8	12.9
AAK-1	1	44.8	8.3
	2	43.6	6.2
AAM-1	1	47.1	9.4
	2	46.1	9.2

Table 6. Viscosities (Pa · s) of Mixtures of Four Core Asphalts with Their IEC Amphoteric, Base, Acid, or Neutral Fractions at 60°C and 1.0 rad/s

Asphalt	Run Number	Viscosity of Asphalt	Viscosity of Asphalt + Amphoterics	Viscosity of Asphalt + Bases	Viscosity of Asphalt + Acids	Viscosity of Asphalt + Neutrals
AAD-1	1	131	2,462	327	174	37
	2	-	2,815	301	211	43
AAG-1	1	240	1,740	346	285	132
	2	-	1,139	402	437	129
AAK-1	1	413	6,836	656	517	110
	2	-	6,755	1,004	550	124
AAM-1	1	258	4,032	399	292	140
	2	-	3,901	470	342	135

Table 7. Viscosities (Pa·s) of Mixtures of Neutral Plus Acid and Base Fractions of Four Asphalts at Three Temperatures Compared with Viscosities of Parent Asphalts

Asphalt	Viscosity of Asphalt (1.0 rad/s)		Tan δ , Asphalt (25°C)	Viscosity of Mixture (1.0 rad/s)		Tan δ , Mixture (25°C)
	25°C	45°C		25°C	45°C	
AAD-1	40,570	1,083	2.60	1,264	54.3	17.09
AAG-1	354,000	3,202	8.91	41,260	559.3	97.85
AAK-1	81,050	4,203	2.47	7,272	220.9	14.01
AAM-1	161,550	2,769	2.31	18,450	318.7	12.48

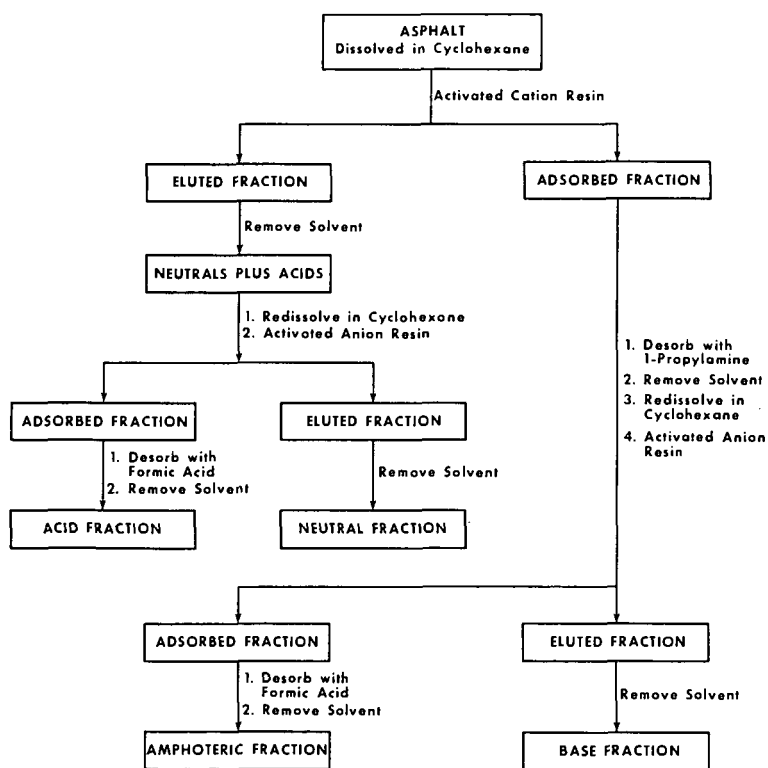


Figure 1. Flow Sheet for Isolation of Amphoteries by IEC